

Eur päisches Patentamt  
European Patent Office  
Office européen des brevets



(11) **EP 0 409 459 B2**

(12) **NEW EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention  
of the opposition decision:  
**22.03.2000 Bulletin 2000/12**

(51) Int. Cl.<sup>7</sup>: **C09D 5/02**

(45) Mention of the grant of the patent:  
**21.05.1997 Bulletin 1997/21**

(21) Application number: **90307464.9**

(22) Date of filing: **09.07.1990**

(54) **Use of aqueous coating compositions**

Verwendung von wässrigen Überzugszusammensetzungen

Utilisation d'une composition de revêtement aqueuse

(84) Designated Contracting States:  
**AT BE CH DE DK ES FR GB GR IT LI LU NL SE**

(30) Priority: **21.07.1989 US 383944**

(43) Date of publication of application:  
**23.01.1991 Bulletin 1991/04**

(73) Proprietor:  
**ROHM AND HAAS COMPANY**  
**Philadelphia Pennsylvania 19105 (US)**

(72) Inventors:  
• **Frank, Landy**  
**Jenkintown, PA 19046 (US)**  
• **Mercurio, Andrew**  
**Gwynedd Valley, PA 19437 (US)**

• **Flynn, Roy**  
**Warrington, PA 19876 (US)**

(74) Representative:  
**Buckley, Guy Jullan et al**  
**ROHM AND HAAS (UK) LTD.**  
**European Operations Patent Department**  
**Lennig House**  
**2 Mason's Avenue**  
**Croydon CR9 3NB (GB)**

(56) References cited:  
**EP-A- 0 009 110** **EP-A- 0 322 188**  
**US-A- 4 054 717**

• **PATENT ABSTRACTS OF JAPAN, vol. 11, no. 229**  
**(C-436)[2676], 25 July 1987**

**EP 0 409 459 B2**

## Description

[0001] This invention concerns the use of aqueous compositions in or as aqueous road or pavement marking paint or other exterior coatings.

[0002] Various attempts to produce an aqueous road-marking paint as a substitute for solvent-based road marking paints have been disclosed in the art. A significant problem has been that the aqueous paints do not dry quickly enough.

[0003] EP-A-0200249 discloses applying an aqueous dispersion of polymer to the road and then contacting the composition with a water soluble salt to cause the coating to dry rapidly and resist washout by a rain shower five minutes after application. This system would require spraying with two compositions which would require the use of extra equipment.

[0004] EP-A-0 066 108 discloses an aqueous road marking composition in which the binder is a mixture of a pure acrylic resin, a carboxylated styrene/dibutyl fumarate copolymer and a polymeric, polyfunctional amine such as polypropylenimine. This application states that the disclosed compositions are not storage stable beyond 48 hours after which more polyfunctional amine must be added to restore activity.

[0005] EP-A-0322188 discloses aqueous coating compositions comprising film forming latex polymer, weak base-functional synthetic latex polymer and volatile base. However the weak base-functional polymer therein is water-insoluble as a consequence of cross linking or high molecular weight.

[0006] In accordance with the present invention, there is provided the use of an aqueous composition comprising:

a) anionically stabilized emulsion polymer having a Tg no lower than 0°C;

b) a polyamine functional polymer

c) a volatile base in an amount such that the composition has a pH where substantially all of the polyamine functional polymer is a non-ionic state, and wherein more than 50% by weight of the polyamine functional polymer will be soluble at pH values of 5 to 7 on evaporation of the volatile base, with the proviso that the polyamine functional polymer is non-cross linked, in or as a road or pavement marking paint or other exterior coatings.

[0007] In the non-ionic state (deprotonated) polyamine interaction with the anionically stabilized emulsion and any other anionic ingredients which may be present in the composition is eliminated. The volatile base must be volatile enough to be released under air dry conditions. The present invention provides a coating composition that dries quickly, develops water resistance soon after application and retains reactivity after storage.

[0008] The invention provides the use of the above aqueous coating composition in or as an aqueous road or pavement-marking paint. The aqueous road or pavement marking paint of the invention can be used to mark lines or symbols on roads, parking lots, walkways, airport runways, etc. of various compositions such as asphaltic, bituminous or concrete paving with or without aggregate filler or top-dressing. This aqueous road-marking paint dries quickly to develop early resistance to washout and tire tread printing.

[0009] The anionically stabilized emulsion polymer can be prepared by known procedures which are published in texts on the subject such as "Emulsion Polymerization: Theory and Practice" by D.C. Blackley published by Wiley in 1975 and "Emulsion Polymerization" by F.A. Bovey et al. published by Interscience Publishers in 1965. Preferably, the anionically stabilized latex polymer is a polymer or copolymer prepared from a monomer system comprising monomers such as methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, decyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate, styrene, butadiene, ethylene, vinyl acetate, vinyl ester of "Versatic" acid (a tertiary monocarboxylic acid having C<sub>9</sub>, C<sub>10</sub> and C<sub>11</sub> chain length, the vinyl ester is also known as "vinyl versatate"), vinyl chloride, vinyl pyridine, vinylidene chloride, acrylonitrile, chloroprene, acrylic acid methacrylic acid, itaconic acid, maleic acid and fumaric acid. Polymers and copolymers prepared from monomer systems comprising monomers such as alpha-beta ethylenically unsaturated monomers and their esters, especially the acrylic and methacrylic esters, are preferred and are preferably prepared by processes given in "Emulsion Polymerization of Acrylic Monomers: May, 1966" published by the Rohm and Haas Company, Philadelphia, Pa., USA.

[0010] The negative charge on the dispersed latex particles is obtained in any of several ways, the most common being the use of anionic surfactants or dispersants as the stabilizer during the emulsion polymerization or added to the emulsion after polymerization. Nonionic surfactants may, of course, also be present in the latex during or after polymerization of these anionically stabilized latexes. The preferred surfactants and dispersants are the salts of fatty rosin and naphthenic acids, condensation products of naphthalene sulfonic acid and formaldehyde of low molecular weight, carboxylic polymers and copolymers of the appropriate hydrophile-lipophile balance, higher alkyl sulfates, such as sodium lauryl sulfate, alkyl aryl sulfonates, such as dodecylbenzene sulfonate, sodium or potassium isopropylbenzene sulfonates or isopropyl naphthalene sulfonates, sulfosuccinates, such as sodium dioctylsulfosuccinate alkali metal higher alkyl sulfosuccinates, e.g. sodium octyl sulfosuccinate, sodium N-methyl-N-palmitoyltaurate, sodium oleyl isethionate, and alkali metal salts of alkylaryl polyethoxyethanol sulfates or sulfonates, e.g. sodium t-octylphenoxy-polyethoxyethyl sulfate having 1 to 5 oxyethylene units.

[0011] Another type of negatively-charged latex is that which is obtained as a result of including in the polymers small amounts of acidic groups, which may be in the salt form, such as an alkali metal or ammonium salt. Examples of such acidic groups are those derived from incorporated initiator fragments, maleic acid, vinyl sulfonic acid, crotonic acid, acrylic acid, methacrylic acid, and itaconic acid. Preferably, the acid monomers are incorporated as an ingredient of the monomer systems which are polymerised to form the latex.

[0012] The polymer must have a glass transition temperature (T<sub>g</sub>) of at least 0°C. Polymers having a T<sub>g</sub> below 0°C are generally not useful since they are too soft, resulting in poor scrub resistance and accelerated dirt pickup.

[0013] The invention may also be practiced using polymers of more complex morphology, such as core-shell particles. These complex polymer morphologies usually display multiple T<sub>g</sub>'s and may display a T<sub>g</sub> value below 0°C as one of its multiple T<sub>g</sub>'s, however the average or effective T<sub>g</sub> of the polymer must be 0°C or above 0°C, i.e. at least 0°C.

[0014] To prepare a storage stable composition of the polyamine polymer and the anionically stabilized emulsion polymer, the polyamine polymer is maintained essentially in a nonionic state by adding a sufficient amount of volatile base to raise the pH of the composition at or near the point at which substantially all the amine functional groups are in a non-ionic state (deprotonation) and therefore do not interact with the anionically stabilized latex. It is believed the volatile base should be present in an amount sufficient to at least deprotonate the conjugate acid of the amine. A starting point estimate of the amount of volatile base required to reach this point can be calculated from the number of equivalents of base needed to neutralize all of the acid groups in the latex (i.e. acid groups from: copolymerized carboxylic-bearing monomer; surfactant; or initiator) and the conjugate acid of the amine base. If the amine is not sufficiently deprotonated, the emulsion will exhibit observable signs of instability over time, such as viscosity increase and microscopically observable "particle rafting", an early stage of aggregation/ gelation. One equivalent of volatile base (based on latex acids and polyamine titers) is usually enough to yield a stable system although higher levels of volatile base (~3 to 4 equivalents) may be necessary for long term stability. Higher amounts of volatile base may be used without departing from the spirit of the invention although the "quick dry" properties of the coating may be reduced. If the equipment used in the process of manufacture presents opportunities for loss of the volatile base by evaporation at any stage from when the volatile base is added until after the product is packaged in a sealed container, the amount of volatile amine loaded to the production equipment should be increased to offset the loss.

[0015] After application, the volatile base evaporates thus lowering the pH of the composition. When the pH of the composition falls to a point where the protonation of the polyamine begins to occur, the polyamine becomes cationic. The quick dry is believed to be initiated by this conversion of the polyamine to a cationic polymer in the presence of the anionically stabilized emulsion polymer, although the exact mechanism that produces the quick-dry property has not been established.

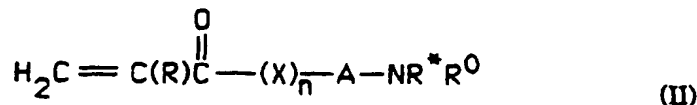
[0016] Preferably, in the polyamine functional polymer, from about 20% to 100%, and preferably at least 50%, by weight of the monomer units which make up the polymer contain an amine group. Examples of the preferred amine containing monomers which are polymerised to form the polyamine functional polymer include members of the following classes:

#### AMINE CLASSES

##### [0017]

1. Aminoalkyl vinyl ethers or sulfides, wherein the alkyl groups may be straight-chain or branched-chain type and have from two to three carbon atoms and wherein the nitrogen atom may be a primary, secondary, or tertiary nitrogen atom (U.S. Pat. No. 2,879,178). In the latter instance, one of the remaining hydrogen atoms may be substituted by alkyl, hydroxyalkyl, or alkoxyalkyl groups, the alkyl components of which may have one to four carbon atoms, preferably one carbon atom only. Specific examples include: beta -aminoethyl vinyl ether; beta -aminoethyl vinyl sulfide; N-monomethyl- beta-aminoethyl vinyl ether or sulfide; N-monoethyl- beta -aminoethyl vinyl ether or sulfide; N-monobutyl- beta -aminoethyl vinyl ether or sulfide; and N-monomethyl-3-aminopropyl vinyl ether or sulfide.

2. Acrylamide or acrylic esters, such as those of the formula II:



wh rein

R is H or CH<sub>3</sub>;  
n is 0 or 1;  
X is O or N(H);

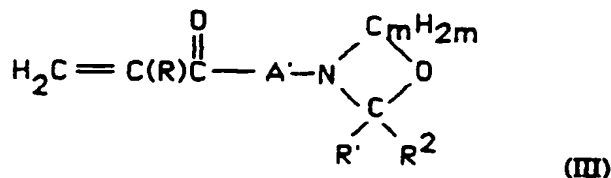
When n is zero, A is O(CH<sub>2</sub>)<sub>x</sub> wherein x is 2 to 3, or (O-alkylene)<sub>y</sub> wherein (O-alkylene)<sub>y</sub> is a poly(oxyalkylene) group, having a molecular weight in the range from 88 to 348, in which the individual alkylene radicals are the same or different and are either ethylene or propylene; and  
when n is 1, A is an alkylene group having two to 4 carbon atoms;

R\* is H, methyl, or ethyl; and  
R<sup>0</sup> is H, phenyl, benzyl, methylbenzyl, cyclohexyl, or (C<sub>1</sub>-C<sub>6</sub>) alkyl.

Examples of compounds of formula II include:

dimethylaminoethylacrylate or methacrylate; beta -aminoethyl acrylate or methacrylate; N- beta -aminoethyl acrylamide or methacrylamide;  
N-(monomethylaminoethyl)-acrylamide or methacrylamide;  
N-(mono-n-butyl)-4-aminobutyl acrylate or methacrylate;  
methacryloxyethoxyethylamine; and acryloxypropoxypropoxypropylamine.

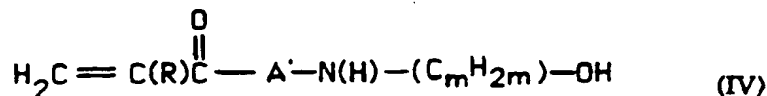
3. N-acryloxyalkyl-oxazolidines and N-acryloxyalkyltetrahydro-1,3-oxazines and the corresponding components in which the "alkyl" linkage is replaced by alkoxyalkyl and poly(alkoxy-alkyl), all of which are embraced by Formula III:



wherein

R is H or CH<sub>3</sub>;  
m is an integer having a value of 2 to 3;  
R<sup>1</sup>, when not directly joined to R<sup>2</sup>, is hydrogen, phenyl, benzyl, or (C<sub>1</sub>-C<sub>12</sub>) alkyl;  
R<sup>2</sup>, when not directly joined to R<sup>1</sup>, is hydrogen or (C<sub>1</sub>-C<sub>4</sub>) alkyl;  
R<sup>1</sup> and R<sup>2</sup>, when directly joined together, form a 5- or 6-carbon ring with the attached carbon atom of the ring in the formula, i.e., R<sup>1</sup> and R<sup>2</sup>, when joined together, are selected from the group consisting of pentamethylene and tetramethylene; and  
A' is O(C<sub>m</sub>H<sub>2m</sub>)- or (O-alkylene)<sub>n</sub> in which (O-alkylene)<sub>n</sub> is a poly(oxyalkylene) group, having a molecular weight in the range from 88 to 348, in which the individual alkylene radicals are the same or different and are either ethylene or propylene.

The compounds of Formula III can hydrolyze under various conditions to secondary amines. The hydrolysis produces products having the Formula IV:



The compounds of Formula III are disclosed in U.S. Pat. Nos. 3,037,006 and 3,502,627, and any of the monomeric compounds disclosed therein may be used in making the copolymers to be used in the composition of the present invention.

Examples of compounds of Formula III include: oxazolidinylethyl methacrylate; oxazolidinylethyl acrylate; 3-(gamma-methacryloxypropyl)-tetrahydro-1,3-oxazine; 3-(beta-methacryloxyethyl)-2,2-penta-methylene-oxazolidine; 3-(beta-methacryloxyethyl)-2-methyl-2-propyloxazolidine; N-2-(2-acryloxyethoxy)ethyl-oxazolidine; N-2-(2-methacryloxyethoxy)ethyl-oxazolidine; N-2-(2-methacryloxyethoxy)ethyl-5-methyl-oxazolidine; N-2-(2-acryloxyethoxy)ethyl-5-methyl-oxazolidine; 3-[2-(2-methacryloxyethoxy)ethyl]-2,2-penta-methylene-oxazolidine; 3-[2-(2-methacryloxyethoxy)ethyl]-2,2-dimethyloxazolidine; 3-[2-(methacryloxyethoxy)ethyl]-2-phenyl-oxazolidine. The polymer is preferably a homopolymer or copolymer comprising units of dimethylaminopropyl-methacrylamide, oxazolidinoethylmethacrylate and/or dimethylaminoethyl-methacrylate, such as polyoxazolidinoethylmethacrylate homopolymer.

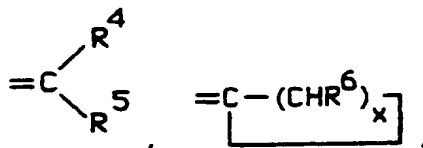
4. Polymers of monomers which readily generate amines by hydrolysis are useful as the amine-containing component or to generate the amine-containing component polymer of this binder composition. Examples of such monomers are acryloxy-ketimines and -aldimines, such as those of Formulas V and VI following:



wherein 3

R is H or CH<sub>3</sub>;

Q is selected from the group consisting of



and = CHR<sup>3</sup>;

R<sup>6</sup> is H or it may be methyl in one CHR<sup>6</sup> unit;

R<sup>5</sup> is selected from the group consisting of (C<sub>1</sub>-C<sub>12</sub>)-alkyl and cyclohexyl groups;

R<sup>4</sup> is selected from the group consisting of (C<sub>1</sub>-C<sub>12</sub>)-alkyl and cyclohexyl

R<sup>3</sup> is selected from the group consisting of phenyl, halophenyl, (C<sub>1</sub>-C<sub>12</sub>)-alkyl, cyclohexyl, and (C<sub>1</sub>-C<sub>4</sub>) alkoxy-phenyl groups;

A<sup>0</sup> is a (C<sub>1</sub>-C<sub>12</sub>) alkylene group;

A<sup>0</sup>, B and D are the same or different oxyalkylene groups having the formula -OCH(R<sup>7</sup>)-CH(R<sup>7</sup>)-wherein R<sup>7</sup> is H, CH<sub>3</sub>, or C<sub>2</sub>H<sub>5</sub>;

x is an integer having a value of 4 to 5;

n' is an integer having a value of 1 to 200;

n is an integer having a value of 1 to 200; and

n is an integer having a value of 1 to 200, the sum of n<sup>0</sup>-1, n'-1 and n"-1 having a value of 2 to 200.

Illustrative compounds of formulas V and VI are:

2-[4-(2,6-dimethylheptylidene)-amino]-ethyl methacrylate  
 3-[2-(4-methylpentylidene)-amino]-propyl methacrylate  
 5 beta-(benzylideneamino)-ethyl methacrylate  
 3-[2-(4-methylpentylidene)-amino]-ethyl methacrylate  
 2-[4-(2,6-dimethylheptylidene)-amino]-ethyl acrylate  
 12-(cyclopentylidene-amino)-dodecyl methacrylate  
 N-(1,3-dimethylbutylidene)-2-(2-methacryloxyethoxy)-ethylamine  
 10 N-(benzylidene)-methacryloxyethoxyethylamine  
 N-(1,3-dimethylbutylidene)-2-(2-acryloxyethoxy)-ethylamine  
 N-(benzylidene)-2-(2-acryloxyethoxy)ethylamine

[0018] The compounds of Formulas V and VI hydrolyze in acid, neutral, or alkaline aqueous media to produce the  
 15 corresponding primary amines or salts thereof in which the group -N = Q of the formulas becomes -NH<sub>2</sub> and O = Q.  
 The compounds of Formulae V and VI are disclosed in U.S. Pat. Nos. 3,037,969 and 3,497,485, and any of the mono-  
 meric compounds therein disclosed may be used in the making of the copolymers to be used in the water-soluble poly-  
 mer portion of the compositions of the present invention.

[0019] Suitable polyamine polymers include both completely soluble and partly soluble polymers. By water-soluble  
 20 amine containing polymer we mean polymer that is completely soluble either in free-base, neutral, or salt form. Some  
 polymers are soluble at all pH's, while others are soluble over a range of pH for example from about 5 to 10. Other  
 amine-containing polymers are generally insoluble at high pH and soluble or partly soluble at acidic pH values, particu-  
 larly in the pH range from about 5 to about 7. By partly soluble is meant both the situation in which some of the polymer  
 25 is soluble in water as well as that in which the entire polymer dissolves in the form of miscelles or aggregates of individ-  
 ual molecules, generally, highly water swollen aggregates. The latter are often called colloidal solutions. For this inven-  
 tion, however, the necessary solubility, as given above, is that most of the polymer is soluble at the acidic pH values (5  
 to 7).

[0020] In general, the amine-containing polymers may be obtained by solution polymerization in aqueous media,  
 either neutral, alkaline, or acidic, depending upon the particular polymer sought, as generally known in the art, for  
 30 example as taught in U.S. Patent 4,119,600. Generally, the polymerization is carried out in an aqueous medium con-  
 taining a small amount of an acid, either organic or inorganic, such as acetic acid or hydrochloric acid. The amine-con-  
 taining polymers include copolymers with up to 80% by weight one or more monoethylenically unsaturated monomers,  
 such as methyl acrylate, acrylamide and methacrylamide. Small amounts of relatively insoluble comonomers may also  
 be used to obtain the water-soluble polymers. The insoluble polymers may contain larger amounts of these comono-  
 35 mers. Such monomers include, as examples, acrylic acid esters with (C1 to C18) alcohols and methacrylic acid esters  
 with alcohols having one to 18 carbon atoms, especially (C1-C4) alkanols; styrene, vinyltoluene, vinyl acetate, vinyl  
 chloride, vinylidene chloride, substituted styrenes, butadiene, substituted butadienes, ethylene; and the nitriles and  
 amides of acrylic or of methacrylic acid. The particular comonomer or comonomers used in making a given amine-con-  
 taining polymer depends upon the proportion of amine-containing monomer used in making the copolymer. The poly-  
 40 mers are thus polymers or copolymers of cationic and, optionally, nonionic vinyl monomers. Examples of the cationic  
 monomers are the amines and imines; the other recited monomers are nonionic. Thus, these water-soluble copolymers  
 contain no acid groups other than trace amounts which may be present due to impurities in the monomers used or to  
 small extent of hydrolysis during synthesis, storage or use.

[0021] Preferably, the amount of polyaminefunctional polymer in the composition is at least 0.25, preferably at least  
 45 0.4 and more preferably at least 0.6, parts per hundred parts emulsion solids by weight. Preferably the amount of  
 polyaminefunctional polymer in the composition is not more than 10 parts, preferably no more than 5 parts and more  
 preferably no more than 2.5 parts, per hundred parts emulsion solids by weight.

[0022] The type and amount of volatile base used must be sufficient to raise the pH of the composition to about the  
 point where the polyamine is substantially non-ionized (deprotonated), to avoid interaction with the anionically stabilized  
 50 emulsion. The volatile base of most preference is ammonia, which may be used as the sole volatile base or in admixture  
 with other volatile or nonvolatile bases. Other preferred volatile bases which may be employed are morpholine, the  
 lower alkyl amines, 2-dimethylaminoethanol, N-methylmorpholine and ethylenediamine.

[0023] Filler, extenders, pigments and other additives known in the art may also be used in the compositions of the  
 invention. If a pigment is used in the traffic paint composition, it is preferably in the range of fifty percent pigment volume  
 content to sixty percent pigment volume content. Examples of pigments that may be employed include clays, calcium  
 55 carbonate, talc, titanium dioxide, carbon black, and various colored pigments.

[0024] Care must be exercised when selecting the type and amount of additives to avoid altering the pH of the com-  
 position to an extent that interferes with storage stability or buffering the pH to an extent that after application the pH

does not fall sufficiently to initiate protonation of the polyamine. For example a paint prepared using a polyamine with a relatively low pKa and too large an amount of calcium carbonate as filler, may display an unacceptably extended cure time.

[0025] Traffic paint compositions typically have a solids content in the range of from thirty five% to seventy% by volume and a viscosity of from about 70 kreb units to about 100 kreb units.

[0026] Coatings provided by the invention are also particularly useful in other exterior coatings such as maintenance coatings, house paint, etc..

[0027] The following examples illustrate some aspects of the invention and should not be construed as limiting the scope of the invention which is described in the specification and claims.

#### Abbreviations:

[0028]

AM = Acrylamide

DMAEMA = Dimethylaminoethylmethacrylate

DMAEMA = Dimethylaminopropylmethacrylamide

HEMA = Hydroxyethylmethacrylate

MMA = Methylmethacrylate

OXEMA = Oxazolidinoethylmethacrylate

p-OXEMA = poly-oxazolidinoethylmethacrylate

#### Paint Preparation

[0029] The test paints were prepared according to the following standard paint formulation by grinding together the ingredients listed as grind ingredients below and then adding the remaining ingredients in the letdown. The emulsion was an anionic copolymer of butyl acrylate, methyl methacrylate and methacrylic acid having a  $T_g$  of 20°C, and a particle size of 200 nanometers.

Grind Ingredient	Amount (lbs/103 gals)
Emulsion (50% solids)	457.9
Water	28.4
Tamol 850 (Rohm and Haas Co.)	7.1
Triton CF-10 (Rohm and Haas Co.)	2.8
Drew L-493	1.0
TiPure R900 (Du Pont)	100.0
Silverbond B	156.3
Snowflake-(calcium carbonate)	595.9
LetDown	
Texanol (Rohm and Haas Co.)	22.9
Methanol	15.0
Drew L-493	2.0
Hydroxyethyl cellulose 250MR (2.5% solution in water)	15.0
	1,404.3

DESCRIPTION OF TEST METHODSDry Time Test

- 5 [0030] This test is similar to ASTM D1640 which is a standard test for drying of organic coatings at room temperature. The test films are applied on a non-porous substrate (glass plate or metal panel) by suitable means to give a wet film thickness of 0.012 +/- 0.001 inches (0.03 +/- 0.0025 cm). The ASTM test method is modified in that only minimal thumb pressure is used. The thumb is turned through an angle of 90° while in contact with the film. The drying time at which this rotation does not break the film is recorded.

10

Early Washout Resistance

- [0031] The test films are prepared in the same manner as for the dry time test. After the films have dried for 15 minutes at a temperature of 78°F (25.5°C) and 50% relative humidity, the samples were held under a stream of cold running water (tap pressure of 170-200 gallons (644-757 l) per hour), which contacted the surface of the paint film at from a nearly perpendicular to an oblique angle. The samples remained under the stream of running water for a period of five (5) minutes. At the end of this period the samples were removed from the test stream and rated by visual inspection. Samples that showed no apparent effect were rated passes; those that exhibited slight disruption of the film were rated marginal; those samples that showed a break in the film or any film removal were rated as fails.

20

Scrub Resistance

- [0032] Films of 3.5 mils (0.009 cm) dry thickness were prepared and cured for 24 hours at 77°F (25°C) +/- 2°F (1°C) and 40-55% relative humidity. The films were tested according to according to ASTM D2486. The number of scrub cycles at which to an area of the paint film was fully removed was recorded.

25

Heat Aging Test

- [0033] One pint (0.5 l) of the test paint was placed in a sealed can and stored in a sealed circulation oven at 120°F (49°C) for one week. The can was removed from the oven and the paint was observed. If the paint is still fluid and shows no apparent signs of bodying or separation it is rated as a pass.

30

EXAMPLES

- 35 Comparative Example A - Addition of Polyamine to Anionic Polymer Latex Produces Paint That Is Not Storage Stable.

[0034] To a paint formulation prepared according to the formulation described above, 10 lbs. (4.5 kg) of polyOXEMA (28.5% solids) was added. The consistency of this paint changed from a fluid mixture to a solidified mass on aging 16 hours at ambient temperature.

40

Example 1- Addition of Volatile Base Produces Paint That Is Storage Stable.

- [0035] The procedure of the Comparative Example was repeated except that 3.9 lbs. (1.75 kg) of ammonium hydroxide (28%) was added before the polyOXEMA. The paint remained fluid when stored at room temperature and passed the heat aging test.

45

Example 2 - Various Levels of Polyamine

- [0036] Test paints were prepared by adding polyamine (polyOXEMA), as in Example 1, in the amount indicated in the table as a percent by weight based on vehicle solids. The paints were applied to substrates and tested. The standard paint without any amine-containing polymer was used as a control. The results appear in the table below:

55

Level of Polyamine (%solids on vehicle solids)	Early Washout Resistance	Scrub Resistance Properties
Control	fail	950 cycle



(continued)

Level of Polyamine (%solids on vehicle solids)	Early Washout Resistance	Scrub Resistance Properties
0.27% p.OXEMA	marginal	--
0.62% p.OXEMA	passes	760 cycles
1.25% p.OXEMA	passes	950 cycles
2.5% p.OXEMA	passes	910 cycles

[0037] The above data demonstrates that the amine-functional polymer produces early washout resistance with acceptable scrub resistance properties. Also, the paint containing 1.25% polyOXEMA dried in 10 minutes in the dry time test compared to 20 minutes dry time for the Control paint that doesn't contain polyamine.

### Example 3 - Use of Polymers and Copolymers of Various Amine-containing Monomers Demonstrated

[0038] Paints were prepared using the indicated amine-containing polymer according to the procedure of Example 1. The paint without any amine-containing polymer was used as a control. Samples were prepared by adding amine-containing polymer to the standard formulation in the amount indicated in the table measured as a percent by weight based on vehicle solids. The sample emulsions were applied to substrates and tested. The results appear in the table below:

Type of Polyamine in marking paint Formulation (1.25% S/S)	Early Washout Resistance	7 days aging 120°F (49°C)
none	fail	passes
pOXEMA	passes	passes
OXEMA/HEMA 50/50	passes	passes
OXEMA/ MMA 70/30	passes	passes
DMAEMA/ AM 70/30	passes	passes
DMAEMA/ HEMA 70/30 (0.44% s/s)	passes	passes
pDMAEMA	passes	passes

[0039] The above data demonstrates that marking paints according to the invention have early washout resistance and were storage stable even under storage at elevated temperature.

### Claims

#### 1. Use of an aqueous composition comprising:

- anionically stabilized emulsion polymer having a Tg no lower than 0°C;
- a polyamine functional polymer
- a volatile base in an amount such that the composition has a pH where substantially all of the polyamine functional polymer is in a non-ionic state, and wherein more than 50% by weight of the polyamine functional polymer will be soluble at pH values of 5 to 7 on evaporation of the volatile base, with the proviso that the polyamine functional polymer is non-crosslinked, in or as a road or pavement marking paint or other exterior coatings.

#### 2. Use as claimed in claim 1 wherein the amount of polyamine functional polymer is from 0.25 to 10 parts per 100 parts emulsion solids by weight, preferably from 0.4 to 5 parts per 100 parts emulsion solids by weight, more preferably from 0.6 to 2.5 parts per 100 parts emulsion solids by weight.

#### 3. Use as claimed in any one of the preceding claims, wherein the polyamine functional polymer comprises units of

dimethylaminopropylmethacrylamide, oxazolidinoethylmethacrylate and/or dimethylaminoethylmethacrylate.

4. Use as claimed in any one of the preceding claims, wherein the polyamine functional polymer is a polymer wherein from 20 percent to 100 percent by weight of monomer units which make up the polymer contain an amine group.
5. Use as claimed in claim 1, wherein the polyamine functional polymer is a polymer or copolymer of cationic and optionally nonionic vinyl monomers, wherein the cationic monomers are imines.

#### Patentansprüche

1. Verwendung einer wäßrigen Zusammensetzung, umfassend:

- a) ein anionisch stabilisiertes Emulsionspolymer mit einer Tg von nicht niedriger als 0°C;
- b) ein polyamin-funktionales Polymer
- c) eine flüchtige Base in einer solchen Menge, daß die Zusammensetzung einen pH aufweist, bei dem im wesentlichen das gesamte polyamin-funktionale Polymer in einem nicht-ionischen Zustand vorliegt, und bei dem mehr als 50 Gew.-% des polyamin-funktionalen Polymers bei pH-Werten von 5 bis 7 aufgrund des Verdampfens der flüchtigen Base löslich sein werden, mit der Maßgabe, daß das polyamin-funktionale Polymer nicht vernetzt ist,
- in oder als ein Straßen- oder Pflastermarkierungsanstrichmittel oder anderen Außenbeschichtungen.

2. Verwendung nach Anspruch 1, bei der die Menge des polyamin-funktionalen Polymers 0,25 bis 10 Teile pro 100 Gewichtsteile Emulsionsfeststoffe, bevorzugt 0,4 bis 5 Teile pro 100 Gewichtsteile Emulsionsfeststoffe, mehr bevorzugt 0,6 bis 2,5 Teile pro 100 Gewichtsteile Emulsionsfeststoffe, beträgt.

3. Verwendung nach einem der vorhergehenden Ansprüche, bei der das polyamin-funktionale Polymer Dimethylaminopropylmethacrylamid-, Oxazolidinoethylmethacrylat-und/oder Dimethylaminoethylmethacrylateinheiten umfaßt.

4. Verwendung nach einem der vorhergehenden Ansprüche, bei der das polyamin-funktionale Polymer ein Polymer ist, in dem 20 bis 100 Gew.-% der Monomereinheiten, welche das Polymer bilden, eine Amingruppe enthalten.

5. Verwendung nach Anspruch 1, wobei das polyamin-funktionale Polymer ein Polymer oder Copolymer von kationischen und gegebenenfalls nichtionischen Vinylmonomeren ist, wobei die kationischen Monomere Imine sind.

#### Revendications

1. Utilisation d'une composition aqueuse comprenant :

- a) un polymère en émulsion, à stabilisation anionique, ayant une Tg non inférieure à 0°C ;
- b) un polymère à fonctionnalité polyamine ;
- c) une base volatile, en une quantité telle que la composition ait un pH pour lequel la quasi-totalité du polymère à fonctionnalité polyamine se trouve dans un état non-ionique, et où plus de 50 % en poids du polymère à fonctionnalité polyamine vont être soluble à des pH de 5 à 7 après évaporation de la base volatile, du moment que le polymère à fonctionnalité polyamine est non-réticulé,
- dans ou en tant que peinture pour le marquage des routes ou des chaussées ou d'autres revêtements extérieurs.

2. Utilisation selon la revendication 1, dans laquelle la quantité du polymère à fonctionnalité polyamine est de 0,25 à 10 parties pour 100 parties en poids d'extrait sec de l'émulsion, de préférence de 0,4 à 5 parties pour 100 parties de l'extrait sec de l'émulsion, plus particulièrement de 0,6 à 2,5 parties pour 100 parties en poids d'extrait sec de l'émulsion.

3. Utilisation selon l'une quelconque des revendications précédentes, dans laquelle le polymère à fonctionnalité polyamine comprend des motifs de diméthylaminopropylméthacrylamide, de méthacrylate d'oxazolidinoéthyle et/ou de méthacrylate de diméthylaminoéthyle.

4. Utilisation selon l'une quelconque des revendications précédentes, dans laquelle le polymère à fonctionnalité polyamine est un polymère dans lequel 20 à 100 % en poids des motifs monomères constituant le polymère contiennent

nent un group amine.

- 5 5. Utilisation selon la revendication 1, dans laquelle le polymère à fonctionnalité polyamine est un polymère ou un copolymère de monomères vinyliques cationiques et éventuellement non-ioniques, dans laquelle les monomères cationiques sont des imines.

10

15

20

25

30

35

40

45

50

55